

**TITLE: LIFE EXTENSION OF CHROMIUM COATINGS AND  
CHROMIUM ALLOYS**

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**FIELD OF THE INVENTION**

The present invention provides a process for treating a chromium alloy or a  
10 chromium coating to (a) increase the hardness of the coating or alloy, and/or (b) to  
increase resistance to friction and wear. The invention also relates to coatings formed  
using the process, which have superior hardness and friction and wear properties.

**BACKGROUND OF THE INVENTION**

Replating of chromium coatings is costly and the effluent from typical  
15 chromium coating processes is toxic to the environment. In fact, environmental  
legislation mandates substantial reductions in chromium plating. As a result,  
processes are needed to prolong the life of chromium coatings and to reduce or  
eliminate the need for stripping, re-plating, and re-machining chromium coated tools.

One relatively low temperature process that is currently used to prolong the  
20 life of chromium coatings is nitrogen ion implantation, which produces a fine  
dispersion of relatively hard and stable chromium nitrides, CrN and Cr<sub>2</sub>N.  
Unfortunately, chromium nitrides are not as hard as many other nitrides. For  
example, CrN has a bulk hardness of only about 11 GPa, or half the hardness of TiN.  
Also, high doses of nitrogen ions are required to produce the chromium nitrides.  
25 Finally, nitrides do not generally have a low coefficient of friction.

Thermally-sprayed chromium oxide has been used to coat bearings, but the  
coating is brittle, is not smooth enough for many applications (such as bearings), and  
presents the problem of decohesion. In addition, thermally-sprayed coatings are

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generally porous and therefore do not provide good corrosion protection for substrates such as steel. A need exists for chromium alloy surfaces and non-porous chromium coatings with increased bulk hardness and low friction and resistance to wear.

**Summary of the Invention**

- 5       In one aspect, the invention provides a method of forming a lubricious outer surface comprising chromium, said method comprising:
- providing a substrate comprising a surface comprising chromium, said surface having an initial coefficient of friction in an unlubricated condition against a steel counterface; and
- 10      treating said substrate with an additive comprising an element X under conditions effective to produce a mixture comprising chromium-X molecules and molecules of said substrate adjacent to said lubricious outer surface, wherein said lubricious outer surface comprises a sufficient quantity of said chromium-X molecules to produce a final coefficient of friction in an unlubricated condition against a steel counterface that is less than said initial coefficient of friction of said surface,
- 15      said additive being selected from the group consisting of substituted or unsubstituted metal carbonyls comprising a metal selected from the group consisting of tungsten, molybdenum, chromium, iron, and nickel, wherein said substituted carbonyls comprise an oxygen of the carbonyl substituted by an element selected from the group consisting of X; and
- 20      compounds having the general formula

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wherein

n is from about 0 to about 6;

m is from about 1 to about 2;

5 o is from about 1 to about 2; and,

X is selected from the group consisting of fluorine, oxygen, sulfur, and chlorine.

In another aspect, the invention provides a variety of substrates comprising a gradient from an inside to an outside surface consisting essentially of:

10 molecules of said substrate/a mixture comprising said substrate molecules and  
said chromium-X molecules/a surface comprising a sufficient quantity  
of said chromium-X molecules to produce a final coefficient of friction  
in an unlubricated condition against a steel counterface that is less than  
a virgin coefficient of friction of said surface in the absence of said  
15 gradient;

wherein X is selected from the group consisting of fluorine, oxygen, sulfur,  
and chlorine.

#### **Detailed Description of the Invention**

Chromium, particularly electroplated chromium, is one of the most important  
20 and widely-used metal coatings. Coatings comprising chromium are used on many  
automotive parts, aeronautical parts, bearings, such as journal bearings, tools for  
injection molding of filled polymers, such as plated molds, tools, runner blocks, and  
the like. Chromium alloys are used in the manufacture of medical devices, such as  
total joint replacements.

- Chromium and its alloys generally comprise an extremely thin film comprising chromium oxide ( $\text{Cr}_2\text{O}_3$ ) at the surface. This film provides lubricity and corrosion resistance. The present invention provides a method to reinforce this chromium oxide and to provide even more resistance to corrosion. The invention
- 5 involves treating a coating comprising chromium to prolong the lifetime of the coating by (a) decreasing the coefficient of friction at the surface and/or (b) increasing the coating hardness. Coatings and chromium alloy surfaces formed using the principles of the present invention exhibit superior friction and wear properties, superior corrosion and pitting resistance, and superior hardness compared to
- 10 chromium coatings and chromium alloy surfaces made or treated using other methods. These superior chromium coatings or chromium alloy surfaces are produced at relatively low temperatures using relatively low dosages of relatively inexpensive “additive.”
- The substrate for a chromium coating typically is a metal or a metal alloy.
- 15 Suitable chromium coatings for treatment according to the invention are formed on a substrate using any known means. Examples include, but are not necessarily limited to electroplating, thermal vapor deposition, sputtering, and pulsed laser deposition. Preferably, the coatings are formed by conventional electroplating. The chromium coating may be a single layer coating, or a multilayered coating. Examples of suitable
- 20 multilayered coatings include, but are not necessarily limited to coatings of alternating layers of Ti and Cr, alternating layers of chromium and amorphous carbon, and the like. Multilayer coatings may be made using any known means, such as alternate vapor or sputter deposition of components.

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- Also suitable for treatment are chromium alloy substrates that containing significant amounts of chromium, preferably at least about 18 percent chromium. In order to be suitable for treatment, the chromium content of any alloy must be sufficiently high to prevent subsequent corrosion of the alloy due to conversion of a percentage of chromium atoms to chromium carbide or chromium oxide. An example of a material not suitable for treatment is stainless steel containing less than about 18% Cr. The conversion of a portion of this relatively low percentage of chromium atoms to carbides may reduce the chromium content of the stainless steel to a point sufficiently low to allow intergranular corrosion.
- The chromium coating or chromium alloy (sometimes collectively referred to as the "substrate") is treated with an "additive." As used herein, the term "additive" is defined as molecules or ions sufficiently small to penetrate a substrate comprising chromium during ion bombardment techniques, and also consisting essentially of components C, X, and optionally H, in the following formula. Suitable additives include, but are not necessarily limited to substituted or unsubstituted metal carbonyls comprising a metal selected from the group consisting of tungsten, molybdenum, chromium, iron, and nickel, wherein said substituted carbonyls comprise an oxygen of the carbonyl substituted by an element selected from the group consisting of X, defined below. Suitable additives also are compounds having the following general formula



wherein n is from about 0 to about 6, m is from about 1 to about 2, and o is from about 1 to about 2, and X is selected from the group consisting of fluorine, oxygen, sulfur, and chlorine. In a preferred embodiment, X is selected from the group

- consisting of fluorine, oxygen, and sulfur. In a most preferred embodiment, X is oxygen. Examples of preferred additives include, but are not necessarily limited to carbon monoxide, carbon dioxide, chromium carbonyl [Cr(CO)<sub>6</sub>], formic acid, methyl alcohol, ethyl alcohol, and acetone. Preferred additives are carbon monoxide and
- 5      carbon dioxide. A most preferred additive for use in ion bombardment techniques, hereinafter sometimes referred to as "penetration" techniques, is carbon monoxide.
- CO<sup>+</sup><sub>2</sub> ions are less toxic than carbon monoxide; however, CO<sup>+</sup><sub>2</sub> ions also are heavier and result in less penetration into a preformed chromium coating or a chromium alloy than the penetration achieved using carbon monoxide ions at the
- 10     same energy. Carbon dioxide ions are preferred in applications where penetration depth is less important, such as where the coating is formed using vapor deposition techniques, and the additive is incorporated into the coating as it is formed.

Where the additive must penetrate a preformed chromium coating or a chromium alloy surface, the additive preferably comprises molecules sufficiently small to penetrate through the chromium coating or alloy surface to within about 100 nm of the substrate under the conditions of activation. Preferably, the additive molecules penetrate at least 50 nm from the outer surface, more preferably at least about 150 nm, and most preferably about 250 nm or more.

The chromium coating or chromium alloy (collectively referred to as the

20     "substrate") is treated with the additive comprising a substituent X under conditions effective to produce a gradient from the inside to the outside surface of the substrate consisting essentially of: substrate molecules/a mixture of substrate molecules and chromium-X molecules/a surface comprising a sufficient quantity of said chromium-X molecules to produce a final coefficient of friction in an unlubricated condition

- against a steel counterface that is less than a virgin coefficient of friction of said surface in the absence of said gradient. In preferred embodiment, X is oxygen, and the gradient consists essentially of: substrate molecules/a mixture of substrate molecules and chromium-oxide molecules/a surface comprising a sufficient quantity
- 5      of said chromium-oxide molecules to produce a final coefficient of friction in an unlubricated condition against a steel counterface that is less than a virgin coefficient of friction of said surface in the absence of said gradient.

To use a penetration technique, the chromium alloy or chromium coating is cleaned using standard methods to remove superficial contaminants, such as grease.

- 10     The substrate is placed in a vacuum chamber that has been evacuated to a base pressure of about  $10^{-5}$  torr or less. The additive ions are energized and contacted with the substrate under conditions effective to cause at least some of the additive ions to penetrate the substrate and to cause at least some of the substituent to chemically react with chromium atoms in the substrate. A preferred technique for energizing the
- 15     additive ions is ion implantation, including but not necessarily limited to direct beam ion implantation and plasma source ion implantation.

A standard ion implantation system consists of a source gas as an ion source; a system to move the ions to the target called the delivery system; and an accelerator, which is the combination of the ion source and the delivery system. During direct

20     beam implantation, positive ions are extracted from a plasma of the desired source gas. An energetic beam of the positive ions may be supplied using any suitable means, including but not necessarily limited to a cold cathode ion source in which the gas or vapor is ionized without the need for high temperatures. Examples are a radio frequency fed ion gun and a twin anode ion source. During plasma source

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implantation, energy is applied to the substrate surface to make that surface the negative electrode of a high voltage system. Positive ions are extracted from the plasma, accelerated toward and penetrate into the substrate surface. Plasmas are generated by glow discharge or radiofrequency means.

- 5        In a preferred embodiment, the substrate is bombarded or irradiated, either in a continuous or interrupted fashion, with an energetic beam of ions of the additive comprising oxygen, most preferably carbon monoxide ions. The energy of the ion beam is sufficient to bring about the necessary quantity of penetration and chemical reaction between substrate atoms and oxygen. Typically, the energy is in the range of  
10      10 from about 500 eV to about 200 keV, preferably from about 20 keV to about 150 keV.

The ion dose is important to the resulting chemical composition. In order to achieve the desired final concentration of additive, the ion dose is from about  $10^{16}$  ions/cm<sup>2</sup> to about  $10^{18}$  ions/cm<sup>2</sup>, and preferably from about  $10^{17}$  ions/cm<sup>2</sup> to about  $3 \times 10^{17}$  ions/cm<sup>2</sup>. A given concentration of oxygen requires approximately twice the  
15      number of carbon monoxide ions as carbon dioxide ions. The duration of bombardment is from about 10 to about 40 minutes. It is preferable that the ion implantation be carried out at temperatures of about 150 °C, preferably about 250 °C in order to avoid softening of the chromium substrate at higher temperatures.  
Implantation at elevated temperature allows for the optimum size and distribution of  
20      oxides of chromium near the surface of the chromium.

Where the additive is carbon monoxide or carbon dioxide, the CO<sup>+</sup> and/or CO<sub>2</sub><sup>+</sup> ions are accelerated by a high voltage source to the target surface. Upon impact with the metal surface, the CO<sup>+</sup> and/or CO<sub>2</sub><sup>+</sup> ions dissociate with momentum shared between the carbon and oxygen ions. Both are very reactive with chromium, and

once equilibrium is reached, stable carbides and oxides of chromium are formed.

Relatively small additions of carbon produce considerable strengthening of a chromium coating. In addition to providing wear resistance, the oxide of chromium is exceptionally hard, with a bulk hardness of about 30 GPa, compared to about 11 GPa  
5 for chromium nitride.

Chromium is highly resistant to corrosion due to a protective, extremely thin film of oxide. During sliding wear, the surface oxide resists metal-to-metal welding asperities and so reduces adhesive wear and friction. Ion-implanted oxygen atoms reinforce the protective mechanisms by providing a sub-surface reservoir of oxide.

- 10 Carbides and nitrides do not have low coefficients of friction against steel. The additives that confer the lowest friction coefficients against steel are those with high electronegativities, including but not necessarily limited to fluorine, oxygen, sulfur, and to some extent chlorine. Oxygen is a preferred additive for use with chromium because chromium oxide is more stable than the compounds formed between  
15 chromium and the other listed additives.

- Preferably a sufficient amount of carbon and/or oxygen is reacted with the chromium coating to reduce the coefficient of friction of the chromium coating or chromium alloy surface from about 0.5 in an unlubricated condition against a steel counterface at a load of about 100 MPa to about 0.3 or less, more preferably to about  
20 0.2 or less, and most preferably to about 0.1 or less. In order to achieve this reduction in coefficient of friction, the final coating preferably is about 10 atomic % to about 40 atomic % oxygen in relation to the chromium content, preferably about 25 atomic % oxygen in relation to the chromium content.

The bulk hardness of chromium nitride is about 11 GPa. Carbon atoms are more effective for hardening a chromium coating or a chromium alloy substrate than nitrogen atoms because carbon atoms are larger and diffuse less rapidly than nitrogen atoms and thus, at a given temperature, cannot segregate so easily to form a second phase carbide precipitate. The local strain introduced into the chromium lattice by introduction of carbon or carbide precipitates is greater than the corresponding local strain for nitrogen precipitates. It is this increased local strain that impedes the movement of dislocations and thereby hardens the material. Furthermore, the precipitates formed by carbides will be smaller than those formed by nitrides under comparable conditions. As a result, the precipitates formed by carbides are more likely to be in an optimum size range of from about 10 atomic % to about 30 nm--a size range of precipitates which maximizes coherency strain and mechanical interaction with any dislocation(s) moving through the chromium lattice. In steel tempered below 300°C, the monoclinic Hägg carbide,  $\text{Fe}_{2.2}\text{C}$ , is formed and is very effective in hardening mechanisms. Another strengthener at low concentrations is  $\text{Fe}_{2.3}\text{C}_5$ . Chromium forms a similar range of carbides to those of iron.

Preferably a sufficient amount of carbon is chemically reacted with the chromium to increase the hardness of the coating to about 15 GPa or more, more preferably about 20 GPa or more, even more preferably to about 25 GPa or more. In order to achieve this level of hardness, the final coating content is preferably from about 10 atomic % to about 30 atomic % carbon in relation to the chromium content, preferably about 20 atomic % carbon in relation to the chromium content.

Persons of ordinary skill in the art will recognize that many modifications may be made to the present invention without departing from the spirit and scope of the

invention. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following claims.